

**B0813**

## **A comparison of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ , $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and $\text{Pr}_2\text{NiO}_{4+\delta}$ cathodes on the performance of anode supported microtubular cells**

**M. A. Laguna-Bercero (1), H. Monzón (1), J. Silva (1), M. J. López-Robledo (1),  
A. Larrea (1), V. M. Orera (1), A. Várez (2), B. Levenfeld (2)**

(1) Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC-Universidad de Zaragoza.

Pedro Cerbuna 12, 50009 Zaragoza, Spain

Tel.: +34-876-55-5152

[malaguna@unizar.es](mailto:malaguna@unizar.es)

(2) Dpto. Ciencia e Ingeniería de Materiales. Universidad Carlos III de Madrid.  
Avda. Universidad 30 28911 Leganés, Spain

### **Abstract**

The performance of YSZ-Ni supported microtubular solid oxide fuel cells (mT-SOFCs) with thin YSZ electrolyte and three different cathodes:  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$  (LSM),  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF) and  $\text{Pr}_2\text{NiO}_{4+\delta}$  (PNO) is compared. The mT-SOFC cells were fabricated using NiO-YSZ support precursors manufactured by Powder Extrusion Moulding (PEM). The YSZ layer was deposited by dip coating. The electrolyte deposition parameters and the sintering parameters were optimized to obtain a dense and thin layer. Three different cathode materials, LSM, LSCF and PNO were then deposited by dip coating. To circumvent reactivity at the sintering temperatures between LSCF and PNO with the YSZ electrolyte, barrier layers were also deposited.

Electrochemical characterization under the same fuelling conditions for all the three cells was performed. The results are discussed and compared. As for example, the cell with a LSM-YSZ cathode presented a power density at 0.5V and 850 °C of 0.7 Wcm<sup>-2</sup> with an ASR (area specific resistance) at OCV (open circuit voltage) of ~0.9 Ωcm<sup>2</sup>. Similar performance was obtained when using LSCF or PNO cathodes at about 750 °C, allowing for a significant reduction of the operation temperature of these mT-SOFCs.

## Introduction

Microtubular SOFCs (mT-SOFCs, inner diameter below ~0.4 millimeters) have been proposed for portable applications, as they admit rapid start-up times and also have much higher volumetric power densities in comparison with standard planar and tubular designs [1,2,3]. Furthermore, mT-SOFCs have also been proposed as solid oxide electrolyzers (SOEC) [4]. As for planar and tubular designs, most used materials for their components are: NiO-YSZ (yttria stabilized zirconia) or NiO-GDC (gadolinia doped ceria) for the anode; YSZ or GDC as the electrolyte; and LSM (lanthanum strontium manganite) or LSCF (lanthanum strontium cobalt ferrite) perovskites for the cathode. Other promising cathode materials are based on the Ruddlesden-Popper phases. In particular, nickelates such as  $\text{Pr}_2\text{NiO}_{4+\delta}$  (PNO) are foreseen as excellent reversible electrodes for reversible fuel cell-electrolyzer operation. Both LSCF and LNO materials are considered MIEC (mixed ionic and electronic conductor) materials, as they exhibit good electronic conductivity due to the metal mixed valence, together with good ion conductivity due to the oxygen overstoichiometry. However, LSCF cathodes show a tendency to react with YSZ electrolytes to form electronic and ionic conduction resistant phases, such as  $\text{La}_2\text{Zr}_2\text{O}_7$  and  $\text{SrZrO}_3$ , at the interface between the cathode and the electrolyte [5,6]. In the case of LNO, the main drawback for the use of these nickelate phases in electrodes is also their reactivity with standard YSZ or GDC electrolytes.

Therefore, when using LSCF or LNO in the electrodes, we need to keep this contamination to the minimum level by using a barrier layer between the electrolyte and the cathode.

In the present work, the performance of YSZ-based mT-SOFC with  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$  (LSM),  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF) and  $\text{Pr}_2\text{NiO}_{4+\delta}$  (PNO) cathode materials will be studied and compared.

## Experimental section

YSZ-NiO support tubes were fabricated by Powder Extrusion Moulding (PEM). Details about PEM fabrication can be found in reference [11]. About 10-15 micron thick YSZ electrolytes were subsequently deposited by dip-coating and sintered at 1500 °C. Finally, LSM-YSZ, LSCF, and PNO suspensions were dip-coated for the about 40 micron thickness cathode. For the LSCF sample, a thin GDC barrier layer (~3 µm) was previously deposited and sintered at 1400 °C, as described in references [12,13]. For the PNO sample, a barrier layer composed of GDC-PNO (80:20 in wt%) was chosen. An example of cells fabricated for this work is shown in figure 1.

SEM analysis was carried out on polished transverse cross-section samples using a Merlin field emission SEM (Carl Zeiss, Germany). Electrochemical studies were performed using a potentiostat/galvanostat/FRA analyzer (Princeton Applied Research, Oak Ridge, USA) at temperatures between 600 °C and 850 °C using RT humidified pure hydrogen at the fuel electrode ( $Q_T = 100$  sccm) and 20% oxygen/ 80% nitrogen ( $Q_T = 100$  sccm) at the oxygen electrode site. Excess hydrogen was used in order to avoid concentration polarization at high current densities. Electrical connections were made using four platinum wires. Au paste (Metalor) was used to improve current collection at the oxygen electrode side. j-V (current density-voltage) measurements were recorded in galvanodynamic mode from OCV down to 0.5 V at a scan rate of 2.5 mA cm<sup>-2</sup> s<sup>-1</sup>. EIS was performed at OCV before and after all potentiodynamic experiments, and using a sinusoidal signal amplitude of 50 mV over the frequency range of 500 kHz to 0.1 Hz.



Fig 1. Anode supported mT-SOFCs using LSM-YSZ for the cathode

## Results

Typical microstructures for the different cells are shown in figure 2. Good adhesion between the electrolyte and the different cathode materials was obtained.

Electrochemical studies were performed for the three different samples. A summary of the electrochemical properties is shown in table 1. LSM-YSZ sample was only characterized at 800 and 850 °C, as the performance of the LSM cathode below 800 °C is very limited.

Table 1. Summary of the electrochemical properties for the different samples

Sample	Temp (°C)	OCV (V)	Current density at 0.7 V (mA·cm <sup>-2</sup> )	Maximum power density (mW·cm <sup>-2</sup> )	ASR (j-V) (Ω·cm <sup>2</sup> )
LSM-YSZ	800	1.108	602	510	0.664
LSM-YSZ	850	1.101	760	720	0.526
LSCF	650	1.131	250	215	1.720
LSCF	700	1.120	440	395	0.954
LSCF	750	1.110	690	640	0.579
LSCF	800	1.102	970	805	0.412
PNO	650	1.130	210	185	2.047
PNO	700	1.121	380	310	1.105
PNO	750	1.109	590	512	0.683
PNO	800	1.098	810	741	0.493

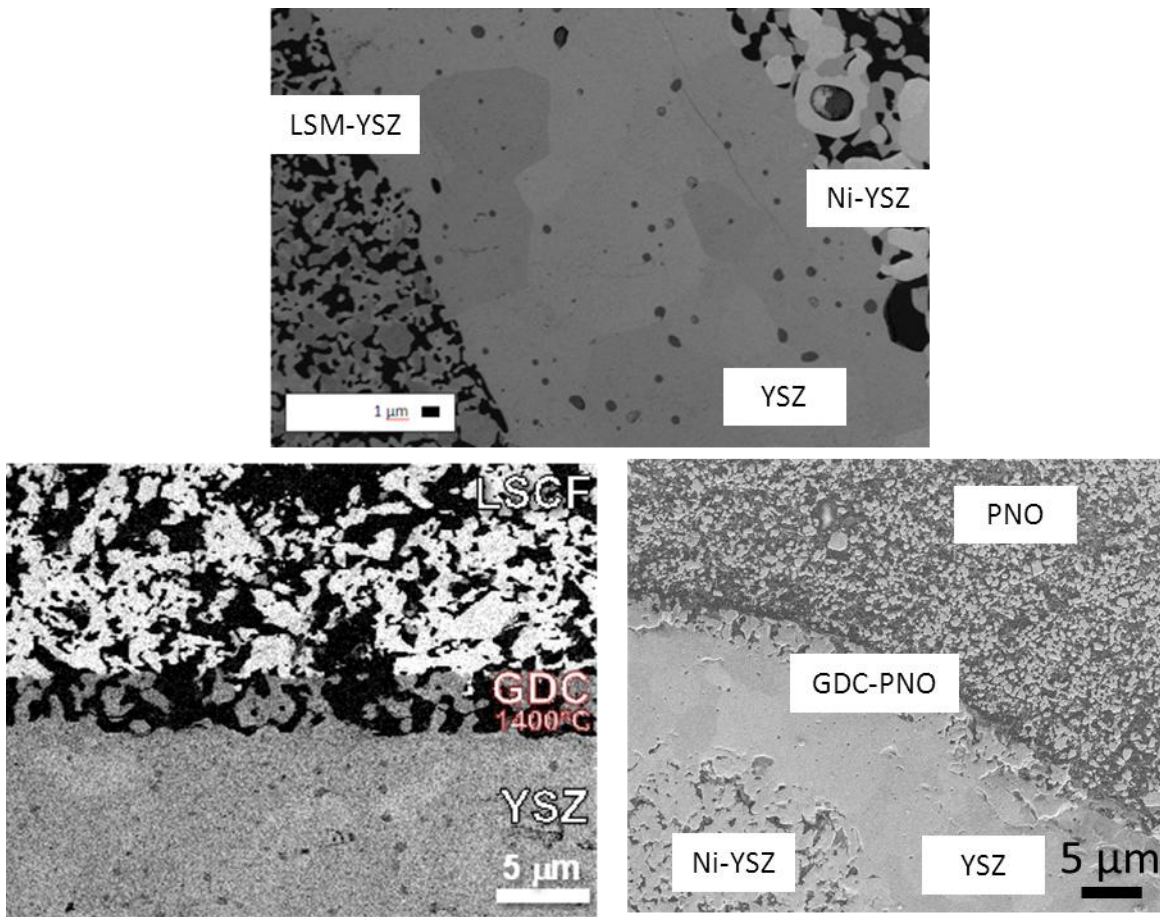


Fig 2. SEM micrographs for the LSM-YSZ cell (up); LSCF cell (bottom left); and PNO cell (bottom right)

As observed from table 2, high OCV values (very close to the theoretical Nernst values) were obtained for the three different cells in the studied temperature range. The performance of the LSM-YSZ cell showed a maximum power density at 0.5V and 800 °C of  $510 \text{ mW}\cdot\text{cm}^{-2}$  and an ASR (area specific resistance) of  $0.66 \text{ }\Omega\cdot\text{cm}^2$ . For the same temperature, cell performance was increased when using PNO cathodes (maximum power density at 0.5 V of  $740 \text{ mW}\cdot\text{cm}^{-2}$  and ASR of  $0.50 \text{ }\Omega\cdot\text{cm}^2$ ), and further increased when using LSCF cathodes (maximum power density at 0.5 V of  $805 \text{ mW}\cdot\text{cm}^{-2}$  and ASR of  $0.40 \text{ }\Omega\cdot\text{cm}^2$ ). EIS experiments performed before and after the electrochemical studies confirmed that there is no apparent cell degradation during operation. In addition, it is very remarkable that the PNO cell showed no degradation during 70 hours under current load.

## Conclusions

The operation temperature of standard YSZ-Ni/YSZ/LSM mT-SOFC cells can be lowered about 100°C when using LSCF and PNO cathodes.

## Acknowledgements

PEM fabrication was made in collaboration with Prof. Alejandro Várez's group (UC3M) for assistance with. Authors also acknowledge grant MAT2012-30763 financed by the Spanish Government (Ministerio de Ciencia e Innovación) and Feder program of the European Community, for funding the project. The use of Servicio General de Apoyo a la Investigación-SAI, Universidad de Zaragoza is finally acknowledged.

## References

- [1] V. Lawlor, *J. Power Sourc.* 2013, 240, 421.
- [2] K. S. Howe, G. J. Thompson, K. Kendall, *J. Power Sourc.* 2011, 196, 1677.
- [3] V. Lawlor, S. Griesser, G. Buchinger, A. G. Olabi, S. Cordiner, D. Meissner, *J. Power Sourc.* 2009, 193, 387.
- [4] M. A. Laguna-Bercero, R. Campana, A. Larrea, J. A. Kilner, V. M. Orera, *J. Electrochem. Soc.* 2010, 6, B852.
- [5] N.Q. Minh, *J. Am. Ceram. Soc.* 76 (1993) 563.
- [6] H.Y. Lee, W.S. Cho, S.M. Oh, *Bull. Korean Chem. Soc.* 19 (1998) 661.
- [7] S. J. Skinner, J. A. Kilner, *Solid State Ionics* 2000, 135, 709.
- [8] F. Mauvy, C. Lalanne, J.-M. Bassat, J.-C. Grenier, H. Zhao, L. Huo and P. Stevens, *J. Electrochem. Soc.* 2006, 153, A1547.
- [9] R. Sayers, J. Liu, B. Rustumji, S. J. Skinner, *Fuel Cells* 2008, 8, 338.
- [10] A. Montenegro-Hernandez, J. Vega-Castillo, L. Mogni, A. Caneiro, *Int. J. Hydrogen Energy* 2011, 36, 15704.
- [11] H. Monzón, M. A. Laguna-Bercero, A. Larrea, B.I. Arias, A. Várez and B. Levenfeld, *Int. J. Hydrogen Energy* 2014, 39, 5470.
- [12] M.J. López Robledo, J. Silva Treviño, T. Molina, R. Moreno. *J. Europ. Ceram. Soc.* 33 (2013) 297-303.
- [13] M.J. López Robledo, M.A. Laguna-Bercero, J. Silva, A. Larrea, V.M. Orera. Submitted to *J. Power Sources*.